

D E C L A R A T I O N

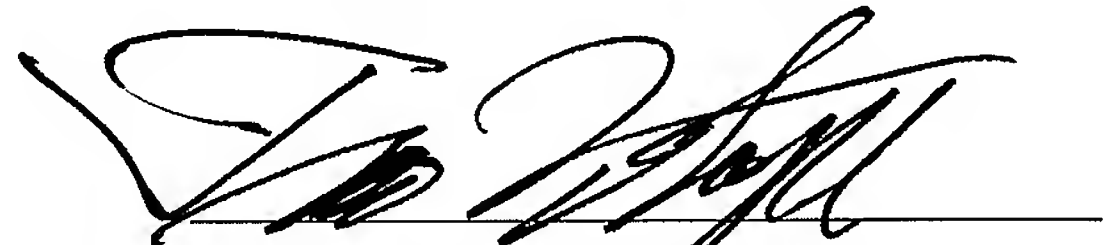
I, TSUNEO KOBAYASHI, a Japanese Patent Attorney registered No.12864 of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No.2003-307618 filed on August 29, 2003 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this

8<sup>th</sup>

day of July, 2008

A handwritten signature in black ink, appearing to read 'Tsuneo Kobayashi', is written over a horizontal line.

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PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application  
as filed with this Office.

Date of Application: August 29, 2003

Application Number: Japanese Patent Application No. 2003-307618

[ST.10/C]: [ JP2003-307618 ]

Applicant(s): CANON KABUSHIKI KAISHA

June 11, 2004

Commissioner,  
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YASUO IMAI (Seal)

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1. Date of Change: August 30, 1990

(Reason of Change) New Registration

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日本国特許庁  
JAPAN PATENT OFFICE

30. 4. 2004

別紙添付の書類に記載されている事項は下記の出願書類に記載されている事項と同一であることを証明する。

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出願人  
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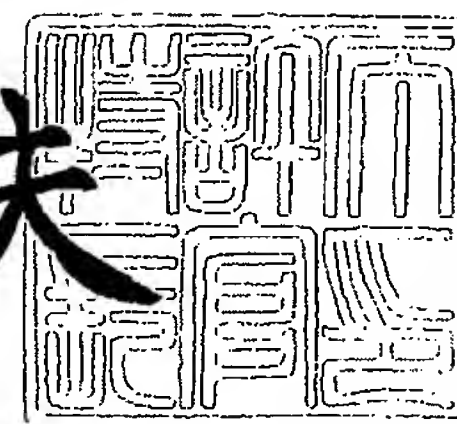
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Japan Patent Office

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[Addressed to] Commissioner, Patent Office  
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[Amount] 21000

[List of Filed Materials]

[Material] Specification 1

[Material] Drawings 1

[Material] Abstract 1

[General Power of Attorney] 9703886

2003-307618

[Name of the Document] Claims

[Claim 1]

A block polymer comprising a repeating unit  
 5 structure comprising an alkenyl ether structure  
 having at least one kind selected from a carboxylic  
 acid, a carboxylic acid ester and a carboxylic acid  
 salt, each having a fluorine atom in a side chain in  
 at least one block segment.

10 [Claim 2]

The block polymer according to claim 1, wherein  
 the pKa of at least one kind selected from the  
 carboxylic acid and the carboxylic acid salt is 2.5  
 or less.

15 [Claim 3]

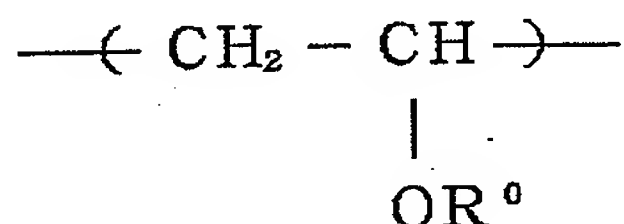
The block polymer according to claim 1 or 2,  
 wherein the block polymer is amphiphilic.

[Claim 4]

The block polymer according to any one of claims  
 20 1 to 3, wherein the repeating unit structure  
 comprising the alkenyl ether structure is represented  
 by the following general formula (1):

[General Formula (1)]

25



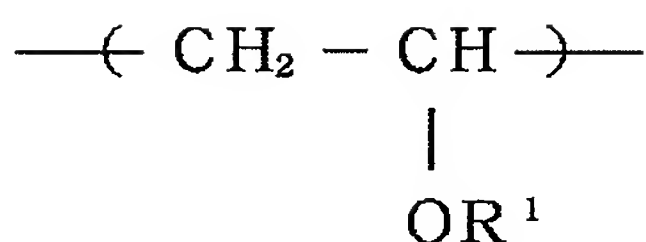


Wherein:  $R^0$  represents  $-X-(Y)_t - (COOH)_r$ ,  $-X-(Y)_t -$   
 5  $(COOR^{10})_r$ ,  $-X-(Y)_t - (COO-M)_r$ , in which X represents  
 a linear, branched or cyclic alkylene group of 1 to  
 20 carbon atoms, or  $-(CH(R^5)-CH(R^6)-O)_p-(CH_2)_m-$   
 $(O)_n-$  or  $-(CH_2)_m-(O)_n-(CH_2)_q-$ , or a structure in which  
 at least one methylene group thereof is replaced by  
 10 an oxygen atom, a carbonyl group or an aromatic ring  
 structure; r represents 1 or 2; p represents an  
 integer of 1 to 20; m represents an integer of 0 to  
 36; n represents 1 or 0; q represents an integer of 0  
 to 20; Y represents an aromatic ring structure in  
 15 which at least one hydrogen atom is substituted with  
 an fluorine atom; t represents an integer of 0 to 10,  
 when t is a plural, Y's may be different from each  
 other;  $R^{10}$  represents an alkyl group or an aromatic  
 ring structure which may be substituted; M represents  
 20 a univalent or multi-valent cation;  $R^5$  and  $R^6$  each  
 represent a hydrogen atom or an alkyl group, and  $R^5$   
 and  $R^6$  may be the same or different from each other.

[Claim 5]

The block polymer according to any one of claims 1  
 25 to 3, comprising the repeating unit structure  
 represented by the general formula (2):

[General Formula (2)]



wherein  $R^1$  is selected from a linear, branched or cyclic alkyl group of 1 to 18 carbon atoms, -Ph, -Pyr, -Ph-Ph, -Ph-Pyr,  $-(\text{CH}(R^5)-\text{CH}(R^6)-\text{O})_p-R^7$  and  $-(\text{CH}_2)_m-(\text{O})_n-R^7$  in which hydrogen atom(s) in the aromatic ring may be substituted with linear or branched alkyl group(s) of 1 to 4 carbon atoms and carbon atom(s) in the aromatic ring may be replaced by nitrogen atom(s);

10  $p$  represents an integer of 1 to 18;

$m$  represents an integer of 1 to 36;

$n$  represents 0 or 1;

$R^5$  and  $R^6$  each represent, independently of one another, a hydrogen atom or  $-\text{CH}_3$ ;

15  $R^7$  is selected from a hydrogen atom, a linear, branched or cyclic alkyl group of 1 to 18 carbon atoms, -Ph, -Pyr, -Ph-Ph, -Ph-Pyr, -CHO,  $-\text{CH}_2\text{CHO}$ ,  $-\text{CO}-\text{CH}=\text{CH}_2$ ,  $-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$ , and  $-\text{CH}_2\text{COOR}_8$ , and when  $R^7$  is other than a hydrogen atom, hydrogen atom(s) attached to carbon atom(s) in  $R^7$  may be substituted with a linear or branched alkyl group of 1 to 4 carbon atoms, -F, -Cl, or -Br, and carbon atom(s) in the aromatic ring may be replaced by nitrogen atom(s);

25  $R^8$  represents a hydrogen atom or an alkyl group of 1 to 5 carbon atoms;

Ph represents a phenyl group; and

Pyr represents a pyridyl group.

[Claim 6]

5 A block polymer having an alkenyl ether repeating unit structure which has an ionic functional group in a side chain in at least one block segment, wherein the pKa of the ionic functional group is 2.5 or less.

[Claim 7]

10 A polymer containing composition comprising the block polymer according to any one of claims 1 to 6, a solvent or dispersion medium, and a functional substance.

[Claim 8]

15 The polymer containing composition according to claim 7, wherein the functional substance is included in the block polymer.

[Claim 9]

20 An ink composition comprising the block polymer according to any one of claims 1 to 6, a solvent or dispersion medium, and a coloring material.

[Claim 10]

25 A liquid application method comprising ejecting a liquid from a liquid ejection portion and applying the liquid to a recording medium to effect recording, wherein the liquid is the polymer containing composition or the ink composition according to any one of claims 7 to 9.

## [Claim 11]

A liquid ejection apparatus, comprising liquid ejection means for applying an energy for ejection to the polymer containing composition or the ink composition according to any one of claims 7 to 9 to eject an ink; and drive means for driving the liquid ejection means.

[Name of the Document] Specification

[Title of the Invention] Block Polymer, Polymer  
Containing Composition Containing the Same, Ink  
Composition, Liquid Application Method, and Liquid

5 Application Apparatus

[Field of the Invention]

[0001]

The present invention relates to a novel block  
polymer which is useful as a functional material, a  
10 polymer containing composition containing the polymer,  
an ink composition, and a liquid application method and  
apparatus using the ink composition.

[Background Art]

[0002]

15 Aqueous dispersion materials containing a  
functional substance have conventionally been known  
widely as functional materials, such as agricultural  
chemicals such as herbicides or insecticides,  
pharmaceuticals such as antitumor agents, antiallergic  
20 agents or antiphlogistics, and coloring materials such  
as ink or toner containing a coloring agent. Digital  
printing techniques have been highly developed in  
recent years. Electrophotography and ink-jet technique  
are representative examples of such digital printing  
25 techniques, and in these years, the presence of such  
techniques have been increasingly enhanced as image  
formation techniques applied both in office and home.

[0003]

Among others, the ink-jet technique is a direct recording method characterized in that it is compact in scale, resulting in low power consumption. In addition,  
5 image quality is being rapidly improved by miniaturization of nozzles or the like. Examples of such ink-jet techniques include a method comprising heating an ink supplied from an ink tank with a heater in a nozzle so as to evaporate the ink and form an ink  
10 bubble, and then ejecting the ink bubble to form an image on a recording medium. Another example is a method of vibrating piezo elements to eject an ink from a nozzle.

[0004]

15 Since an aqueous dye solution has been commonly used as ink used in these methods, there have been some cases where smearing has been occurred, or a phenomenon called feathering has been appeared in the fiber direction of paper at a recording area on a recording  
20 medium, when different colors were overlaid. The use of pigment dispersion ink has been studied to improve the above problems (Patent Document 1). However, it is still desired that many other improvements have been made for such ink.

25 [Patent Document 1] U. S. Patent No. 5,085,698

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0005]

The present invention has been accomplished in view of the above mentioned problems of the background art as mentioned above. Accordingly, the present invention aims to provide a block polymer capable of satisfactorily dispersing a functional substance in a solvent.

Further, the present invention also aims to provide a polymer containing composition which contains the block polymer mentioned above and has a good dispersion property for a functional substance.

[0006]

Moreover, the present invention further aims to provide an ink composition containing the block polymer mentioned above and having a good dispersion property of a coloring material.

Further, the present invention still further aims to provide a liquid application method and apparatus for stably eject the composition having the good dispersion property.

[Means for Solving the Problems]

[0007]

The above problems can be solved by the present invention which will be described below.

The present invention provides a block polymer including a repeating unit structure including an alkenyl ether structure having at least one kind

selected from a carboxylic acid, a carboxylic acid ester and a carboxylic acid salt, each having a fluorine atom in a side chain in at least one block segment.

5 [0008]

The present invention provides a polymer containing composition which contains the above mentioned block polymer, a solvent or dispersion medium, and a functional substance.

10 The present invention provides an ink composition which contains the above mentioned block polymer, a solvent or dispersion medium, and a coloring material.

[0009]

The present invention provides a liquid  
15 application method which includes ejecting a liquid from a liquid ejection portion and applying the liquid to a recording medium to effect recording, wherein the liquid is the above-mentioned polymer containing composition or the ink composition.

20 [0010]

The present invention provides a liquid ejection apparatus which includes liquid ejection means for applying an energy for ejection to the above-mentioned polymer containing composition or the ink composition  
25 to eject an ink, and drive means for driving the liquid ejection means.

[0011]



The present invention provides a block polymer having an alkenyl ether repeating unit structure which has an ionic functional group in a side chain in at least one block segment, wherein the pKa of the ionic  
5 functional group is 2.5 or less.

[Effect of the Invention]

[0012]

According to the present invention, there can be provided a block polymer capable of satisfactorily  
10 dispersing a functional substance in a solvent.

According to the present invention, there can be also provided a polymer containing composition which contains the above mentioned block polymer and having a good dispersion property for the functional substance.  
15 [0013]

According to the present invention, there can be further provided an ink composition containing the above mentioned block polymer and having a good dispersion property for a coloring material.

20 According to the present invention, there can be further provided a liquid application method and apparatus for stably ejecting the above mentioned composition with the good dispersion property.

[Best Modes for Carrying Out the Invention]

25 [0014]

Next, the present invention will be described in detail.

A first aspect of the present invention is a block polymer including a repeating unit structure including an alkenyl ether structure having at least one kind selected from a carboxylic acid, a carboxylic acid ester and a carboxylic acid salt, each having a  
5 fluorine atom in a side chain in at least one block segment. Preferably, the pKa of the carboxylic acid or the carboxylic acid salt is 2.5 or less.

[0015]

10 The term "block polymer" herein employed refers to a copolymer in which a plurality of different kinds of block segments are coupled to one another on a polymer chain, and is also referred to as a block copolymer.

[0016]

15 The present invention also provides a block polymer having an alkenyl ether repeating unit structure which has an ionic functional group in a side chain in at least one block segment, in which the pKa of the ionic functional group is 2.5 or less.

20 [0017]

An aromatic carboxylic acid in which hydrogen atom(s) is substituted with fluorine atom(s) has an effect of stabilizing the anion (carboxylic acid ion) by substitution with fluorine atom(s) which is an  
25 electron attractive group. Therefore, the block polymer of the present invention is useful in that protons in the carboxylic acid or metal ions in the carboxylic

acid salt are liable to be released in an aqueous solution, and hence the acidity is increased (pKa is reduced), that is, unlike the acidity of other carboxylic acids, the acidity and the degree of dissociation are high as a polymer compound and hence various functional properties can be exhibited.

[0018]

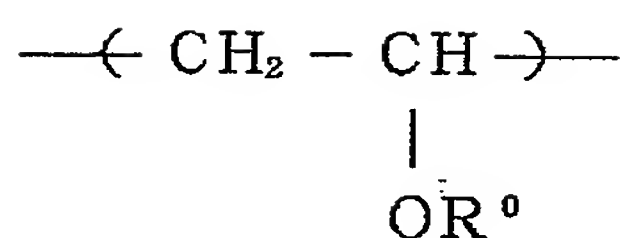
In addition, a favorable aspect of the block polymer of the present invention is an amphiphilic compound. Another favorable aspect thereof is a compound containing a polyalkenyl ether structure as a repeating unit structure and a further favorable aspect is a compound containing a polyvinyl ether structure as a repeating unit structure.

[0019]

As a specific example of the block polymer of the present invention, a compound containing the polyvinyl ether structure as the repeating unit structure can be given as a favorable example. In addition, the repeating unit structure having the carboxylic acid, the carboxylic acid ether or the carboxylic acid salt, each having the fluorine atom in the side chain is a repeating unit structure represented by the following general formula (1) and a compound containing this repeating unit structure is favorable.

[0020]

[General formula (1)]



5

[0021]

wherein:  $R^0$  represents  $-X-(Y)_t - (\text{COOH})_r$ ,  $-X-(Y)_t -$   
 10  $(\text{COOR}^{10})_r$ ,  $-X-(Y)_t - (\text{COO-M})_r$ , in which X represents  
 a linear, branched or cyclic alkylene group of 1 to  
 20 carbon atoms, or  $-(\text{CH}(R^5) - \text{CH}(R^6) - \text{O})_p - (\text{CH}_2)_m -$   
 $(\text{O})_n -$  or  $-(\text{CH}_2)_m - (\text{O})_n - (\text{CH}_2)_q -$ , or a structure in which  
 at least one methylene group thereof is replaced by  
 15 an oxygen atom, a carbonyl group or an aromatic ring  
 structure; r represents 1 or 2; p represents an  
 integer of 1 to 20; m represents an integer of 0 to  
 36; n represents 1 or 0; q represents an integer of 0  
 to 20; Y represents an aromatic ring structure in  
 20 which at least one hydrogen atom is substituted with  
 an fluorine atom; t represents an integer of 0 to 10,  
 when t is a plural, Y's may be different from each  
 other;  $R^{10}$  represents an alkyl group or an aromatic  
 ring structure which may be substituted; M represents  
 25 a univalent or multi-valent cation;  $R^5$  and  $R^6$  each  
 represent a hydrogen atom or an alkyl group, and  $R^5$   
 and  $R^6$  may be the same or different from each other.

[0022]

Specific examples of the repeating unit structures represented by the general formula (1) will be given below.

5           Incidentally, the structures of only  $-OR^{\circ}$  group in a side chain bonded to  $-(CH_2-CH)-$  of the repeating unit structure represented by the general formula (1) will be shown below.

[0023]

10

15

20

25

	$\text{OCH}_2\text{CH}_2\text{OPh (4F) COOC}_2\text{H}_5$
	$\text{OCH}_2\text{CH}_2\text{OPh (4F) COOH}$
	$\text{OCH}_2\text{CH}_2\text{OPh (4F) COO}^- \text{Na}^+$
5	$\text{OCH}_2\text{CH}_2\text{Ph (3F) COOCH}_3$
	$\text{OCH}_2\text{CH}_2\text{OPh (F) COOC}_2\text{H}_5$
	$\text{OCH}_2\text{CH}_2\text{ONp (2F) COOC}_2\text{H}_5$
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OPh (F) COOC}_2\text{H}_5$
10	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OPh (3F) COOCH}_3$
	$\text{OCH}_2\text{CH (CH}_3\text{) OPh (3F) COOC}_2\text{H}_5$
	$\text{OCH}_2\text{CH (C}_2\text{H}_5\text{) OPh (3F) COO}^- \text{Na}^+$
	$\text{OCH}_2\text{CH (C}_3\text{H}_7\text{) OPh (3F) COOC}_2\text{H}_5$
	<del><math>\text{O (CH}_2\text{CH}_2\text{O)}_2\text{Ph (3F) COOC}_3\text{H}_7</math></del>
15	$\text{O (CH}_2\text{CH}_2\text{O)}_2\text{Ph (2F) COOCH}_3$
	$\text{O (CH}_2\text{CH}_2\text{O)}_2\text{Ph (2F) COOC}_2\text{H}_5$
	<del><math>\text{O (CH}_2\text{CH}_2\text{O)}_3\text{Ph (4F) COOC}_2\text{H}_5</math></del>
	$\text{O (CH}_2\text{CH}_2\text{O)}_2\text{Np (F) COOC}_2\text{H}_5$
20	$\text{O (CH}_2\text{CH}_2\text{O)}_3\text{Np (4F) COOC}_2\text{H}_5$
	$\text{O (CH}_2\text{CH}_2\text{O)}_3\text{Np (5F) COOH}$
	$\text{OCH}_2\text{CH}_2\text{O (CH}_2\text{)}_2\text{Ph (3F) COOCH}_3$
	$\text{OCH}_2\text{CH}_2\text{O (CH}_2\text{)}_3\text{Ph (3F) COO}^- \text{K}^+$
	$\text{OCH}_2\text{CH}_2\text{O (CH}_2\text{)}_4\text{PhPh (3F) COOCH}_3$
25	$\text{OCH}_2\text{CH}_2\text{O (CH}_2\text{)}_5\text{Np (3F) COOCH}_3$

[0024]

	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_5\text{Ph} (3\text{F}) \text{COOCH}_3$
5	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_7\text{PhPh} (3\text{F}) \text{COO}^- \text{K}^+$
	$\text{OCH}_2\text{CH}_2\text{O} (\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{Ph} (3\text{F}) \text{COOCH}_3$
	$\text{OCH}_2\text{CH}_2\text{OPyPh} (2\text{F}) \text{COOCH}_3$
	$\text{OCH}_2\text{CH}_2\text{OPyPh} (2\text{F}) \text{COO}^- \text{Li}^+$
10	$\text{OCH}_2\text{CH}_2\text{O} (\text{CH}_2)_{20}\text{Ph} (2\text{F}) \text{COOCH}_3$
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_2 (\text{CH}_2)_2\text{Ph} (2\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_3 (\text{CH}_2)_3\text{Ph} (2\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_{10}\text{Ph} (2\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_{20}\text{Ph} (2\text{F}) \text{COOH}$
15	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_2 (\text{CH}_2)_6\text{OPh} (2\text{F}) \text{COOC}_2\text{H}_5$
	<del><math>\text{O} (\text{CH}_2\text{CH}_2\text{O})_5 (\text{CH}_2)_7\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5</math></del>
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_6 (\text{CH}_2)_8\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_{10} (\text{CH}_2)_{10}\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5$
20	<del><math>\text{O} (\text{CH}_2\text{CH}_2\text{O})_{15} (\text{CH}_2)_{15}\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5</math></del>
	$\text{O} (\text{CH}_2\text{CH}_2\text{O})_2 (\text{CH}_2)_{20}\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2)_8\text{O} (\text{CH}_2)_2\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2)_4\text{O} (\text{CH}_2)_3\text{OPh} (3\text{F}) \text{COOC}_2\text{H}_5$
25	$\text{O} (\text{CH}_2)_4\text{O} (\text{CH}_2)_4\text{OPh} (4\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2)_8\text{O} (\text{CH}_2)_5\text{OPh} (4\text{F}) \text{COOC}_2\text{H}_5$
	$\text{O} (\text{CH}_2)_6\text{O} (\text{CH}_2)_6\text{OPh} (4\text{F}) \text{COOC}_2\text{H}_5$
	$\text{OCH} (\text{CH}_3)\text{CH}_2\text{O} (\text{CH}_2)_7\text{OPh} (4\text{F}) \text{COOC}_2\text{H}_5$

[0025]

	<del>OCH (CH<sub>3</sub>)CH<sub>2</sub>O (CH<sub>2</sub>)<sub>8</sub>OPh (4F) COOH</del>
5	<del>OCH<sub>2</sub>CH (CH<sub>3</sub>)O (CH<sub>2</sub>)<sub>10</sub>OPh (4F) COOC<sub>2</sub>H<sub>5</sub></del>
	<del>OCH(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>O (CH<sub>2</sub>)<sub>15</sub>OPh (4F) COOC<sub>2</sub>H<sub>5</sub></del>
	<del>OCH<sub>2</sub>CH (CH<sub>3</sub>)O (CH<sub>2</sub>)<sub>20</sub>OPh (2F) COOC<sub>2</sub>H<sub>5</sub></del>
	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>2</sub>OPh (3F) COOPhH</del>
10	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>3</sub>OPh (3F) COOCH<sub>2</sub>PhH</del>
	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>4</sub>OPh (4F) COOPyrH</del>
	<del>O (CH<sub>2</sub>)<sub>4</sub>O (CH<sub>2</sub>)<sub>5</sub>OPyr (3F) COOPhH</del>
	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>6</sub>OPh (3F) COOPh (OCH<sub>3</sub>)</del>
	<del>O (CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub> (CH<sub>2</sub>)<sub>7</sub>OPh (F) COOPh (OCH<sub>3</sub>)</del>
15	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>8</sub>OPh (4F) COOPh (OCH<sub>3</sub>)</del>
	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>10</sub>OPh (4F) COOPh (OCH<sub>3</sub>)</del>
	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>15</sub>OPh (2F) COOPh (OCH<sub>3</sub>)</del>
	<del>OCH<sub>2</sub>CH<sub>2</sub>O (CH<sub>2</sub>)<sub>20</sub>OPh (2F) COOPh (OCH<sub>3</sub>)</del>
20	

25



[0026]

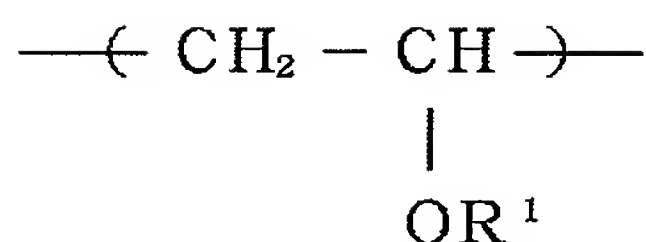
In the above examples, Ph represents 1,4-phenylene or 1,3-phenylene, Py represents 2,5-pyrimidylene, and Pyr represents 2,5-pyridylene. Np represents 2,6-naphthyl, 1,4-naphthyl or 1,5-naphthyl. The expression Ph (F) represents 2- or 3-monofluoro substitution. The expression Ph (2F) represents 2,3-, 2,6-, 2,5- or 3,5-difluoro substitution. The expression Ph (3F) represents 2,3,5- or 2,3,6-trifluoro substitution. The expression Ph (4F) represents 2,3,5,6-tetrafluoro substitution. In the case of other aromatic ring structures also, the arabic numeral in parentheses represents the number of fluorine atoms for substitution and indicates that the substitution is effected at any positions.

[0027]

The block polymer of the present invention does not only have a block segment containing the repeating unit structure represented by the above general formula (1), but also have a block segment containing at least another repeating unit structure. More specifically, a block segment containing a repeating unit represented by the following general formula (2) is preferably used:

[0028]

[General Formula (2)]



[0029]

wherein  $R^1$  is selected from the group consisting of a linear, branched or cyclic alkyl group of 1 to 18 carbon atoms, -Ph, -Pyr, -Ph-Ph, -Ph-Pyr,  $-(\text{CH}(R^5)-\text{CH}(R^6)-\text{O})_p-R^7$  and  $-(\text{CH}_2)_m-(\text{O})_n-R^7$ , and hydrogen atom(s) in the aromatic ring may be replaced by linear or branched alkyl group(s) of 1 to 4 carbon atoms, and carbon atom(s) in the aromatic ring may be replaced by nitrogen atom(s);

[0030]

$p$  represents an integer of 1 to 18;

$m$  represents an integer of 1 to 36;

$n$  represents 0 or 1;

each of  $R^5$  and  $R^6$  represents independently a hydrogen atom or  $-\text{CH}_3$ ;

$R^7$  is selected from the group consisting of a hydrogen atom, a linear, branched or cyclic alkyl group of 1 to 18 carbon atoms, -Ph, -Pyr, -Ph-Ph, -Ph-Pyr, -CHO,  $-\text{CH}_2\text{CHO}$ ,  $-\text{CO}-\text{CH}=\text{CH}_2$ ,  $-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$  and  $-\text{CH}_2\text{COOR}_8$ , and when  $R^7$  is other than a hydrogen atom, hydrogen atom(s) attached to carbon atom(s) in  $R^7$  may be replaced by a linear or branched alkyl group of 1 to 4 carbon atoms, -F, -Cl or -Br, and carbon atom(s) in the aromatic ring may be replaced by nitrogen atom(s);

$R^8$  represents a hydrogen atom or an alkyl group of 1 to 5 carbon atoms;

Ph represents a phenyl or phenylene group; and

Pyr represents a pyridyl group.

5 [0031]

Specific examples of the  $R^1$  structure represented by the general formula (2) are as follows:

Incidentally, the structure of only the  $-OR^1$  group in the side chain bonded to  $-(CH_2)-CH)-$  of the repeating unit structure represented by the general formula (2) is shown below.

[0032]

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25

[0033]

In the above examples, Ph represents a phenyl or

phenylene group.

Moreover, each block segment of the block polymer of the present invention may consist of a single kind repeating unit, or may consist of multiple kinds of repeating unit structures. Examples of a block segment consisting of multiple kinds of repeating units include a random copolymer and a graduation copolymer whose compositional ratio is gradually changed. Furthermore, the block polymer of the present invention is a block polymer having two or more block segments and may also be a graft polymer obtained by graft binding of the above block polymer to other polymers.

[0034]

In the present invention, the content of the repeating unit structure represented by the general formula (1) is preferably within the range of 0.01 to 99 mol%, more preferably within the range of 1 to 90 mol% on the basis of the whole block polymer. When the above content is within the range of 0.01 and 99 mol%, carboxylic acid moieties can interact so well with each other that they may function sufficiently, which is preferable.

[0035]

The number-average molecular weight ( $M_n$ ) of the block polymer of the present invention is not less than 200 but no more than 10,000,000, and the range preferably used is not less than 1,000 but no more than

1,000,000. When the number-average molecular weight is not less than 200 but no more than 10,000,000, it causes less entanglement or twisting in a polymer chain or between polymer chains, so that the polymer is easily dispersed in a solvent and can sufficiently exhibit the steric effect as a polymer.

[0036]

The polymerization degree of each block segment is preferably not less than 3 but no more than 10,000, more preferably not less than 5 but no more than 5,000, and most preferably not less than 10 but no more than 4,000.

Further, in order to improve the dispersion stability and the inclusion property (encapsulation property), it is preferable that the molecular motion of the block polymer is more flexible. This is because when the molecular motion of the block polymer is flexible, the block polymer easily becomes entangled (or intertwined) physically with the surface of a functional substance to have a high affinity therewith, and also because a coating layer is easily formed on a recording medium. On this account, the glass transition temperature  $T_g$  of the main chain of the block polymer is preferably 20°C or less, more preferably 0°C or less, and further more preferably -20°C or less. In this respect also, the polymer having a polyvinyl ether structure is preferably used because it generally has a

low glass transition temperature and flexible characteristics. In the above described examples of the repeating unit structures, their glass transition temperature is approximately  $-20^{\circ}\text{C}$  or less in most cases.

5 [0037]

In a preferred embodiment, the block polymer of the present invention is an amphiphilic polymer. When at least one block segment is solvophobic and at least one block segment is solvophilic in the block polymer of the present invention, amphiphilicity develops. As a solvent with regard to which the solvophobicity and solvophilicity are exhibited, an aqueous solvent is preferably used. In other words, the block polymer of the present invention preferably has at least one hydrophobic segment and at least one hydrophilic segment. For example, the hydrophobic segment is a structure represented by the general formula (2) wherein  $\text{R}^1$  is an alkyl group or phenyl group, and the hydrophilic segment has a carboxylic acid or a carboxylic acid salt in a structure represented by  $\text{R}^0$  in the general formula (1).

10  
15  
20

[0038]

Moreover, the block polymer of the present invention is preferably a block polymer comprising a polyalkenyl ether repeating unit comprising at least one selected from a carboxylic acid, a carboxylic acid ester and a carboxylic acid salt, each having a

25

fluorine atom in a side chain thereof in at least one block segment. Furthermore, when the above structure is a fluorine-substituted aromatic carboxylic acid structure, the pKa of the carboxylic acid is preferably 2.5 or less. The fact that the pKa is 2.5 or less means that the compound can sufficiently be in a dissociative state up to a pH close to 3, which shows extremely stable ionicity and hydrophilicity. It is to be noted that pKa is an acid dissociation index and represents the logarithmic value of the reciprocal of an acid dissociation constant Ka. When the concentration of a certain acid (HA) that is not dissociated in a solution is defined as [HA], and when the concentration of a dissociated acid H<sup>+</sup> and the concentration of its counterion are defined as [H<sup>+</sup>] and [A<sup>-</sup>], respectively, the acid dissociation constant Ka is expressed as  $Ka = \frac{[H^+][A^-]}{[HA]}$ . Accordingly, pKa is obtained by the following expression:  $pKa = -\log [H^+] - \log ([A^-]/[HA]) = pH - \log ([A^-]/[HA])$ .

[0039]

Incidentally, although the block polymer of the present invention has the alkenyl ether repeating unit structure having an ionic functional group in a side chain in at least one block segment in which the pKa of the ionic functional group is 2.5 or less, the term "ionic functional group" herein employed means a functional group which ionizes in a solution, such as a

carboxylic acid group.

[0040]

Polymerization of the block polymer of the present invention is mainly a cationic polymerization. Examples  
5 of an initiator used herein include a protonic acid such as hydrochloric acid, sulfuric acid, methanesulfonic acid, trifluoroacetic acid, trifluoromethanesulfonic acid or perchloric acid, or a combination of a Lewis acid such as  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  
10  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{RAlCl}_2$  or  $\text{R}_{1.5}\text{AlCl}_{1.5}$  (wherein R represents alkyl), with a cation source (wherein examples of such a cation source include a protonic acid, and an adduct obtained from water, alcohol, vinyl ether and a carboxylic acid). By making such an initiator coexist  
15 with the polymeric compound (monomer), a polymerization reaction will proceed to synthesize the block polymer.

[0041]

A polymerization method that is more preferably used in the present invention will be explained below.  
20 There have been many reports on methods of synthesizing a polymer containing a polyvinyl ether structure. Among others, the cationic living polymerization method according to Aoshima et al. is representative (Polymer Bulletin Vol. 15, 1986, p.417; and Japanese Patent  
25 Application Laid-Open Nos. H11-322942 and H11-322866). By synthesizing a polymer by the cationic living polymerization, various polymers such as a homopolymer,



copolymer consisting of two or more component monomers, as well as block polymer, graft polymer, graduation polymer, and the like can be synthesized while making their lengths (molecular weights) equal. Moreover, the  
5 living polymerization can also be carried out with an HI/I<sub>2</sub> system or HCl/SnCl<sub>4</sub> system.

[0042]

The second aspect of the present invention is a polymer containing composition which includes a solvent  
10 or dispersion medium, a functional substance, and the above mentioned polymer. The polymer containing composition of the present invention also contains the above mentioned polymer and a functional substance having a useful predetermined function such as a  
15 coloring material and the above mentioned block polymer can be preferably used to satisfactorily disperse the functional substance. The functional substances are preferably liquids and solids and may be soluble substances. For example, oils, pigments, metals,  
20 herbicides, insecticides, biological materials, medicines, dyes, molecular catalysts and the like may be used.

[0043]

The amount of the block polymer contained in the  
25 polymer containing composition of the present invention is within a range from 0.1 to 99 mass% relative to the total weight of the composition, and preferably within a

range from 0.3 to 70 mass%. When the content is within the range from 0.1 to 99 mass%, the functional substance has sufficient dispersion property and hence a favorable viscosity can be attained.

5 [0044]

The amount of the functional substance contained in the polymer containing composition of the present invention is within a range from 0.1 to 80 mass%, and preferably within a range from 0.5 to 60 mass %. When  
10 the content is within the range from 0.1 to 80 mass%, favorable functionality and favorable dispersion property can be exhibited.

[0045]

The polymer containing composition of the present  
15 invention contains a solvent or dispersion medium. A binder resin may be used as the dispersion medium. As the solvent or dispersion medium, water, aqueous solvents, non-aqueous organic solvents and the like may be used. Mixtures thereof may be also used.

20 [0046]

Examples of the aqueous solvent used in the invention include: polyvalent alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, polypropylene  
25 glycol or glycerol; polyvalent alcohol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether,

diethylene glycol monoethyl ether or diethylene glycol monobutyl ether; and nitrogen-containing solvents such as N-methyl-2-pyrrolidone, substituted pyrrolidone or triethanolamine. In addition, monovalent alcohols such as methanol, ethanol or isopropyl alcohol can also be used. As non-aqueous solvents, hydrocarbon based solvents such as hexane, heptane, octane, decane and toluene, and solvents such as cyclohexane, acetone, methyl ethyl ketone and butyl acetate may be used. In addition, natural fats and oils such as olive oil, soybean oil, beef tallow and lard may be used. As examples of binder resins, styrene acryl copolymers and polyesters can be mentioned.

[0047]

The amount of the solvent or dispersion medium contained in the polymer containing composition of the present invention is within a range from 1 to 99 mass%, preferably within a range from 10 to 95 mass%. When the content is within the range from 1 to 99 mass%, the functional substance is sufficiently dispersed.

[0048]

Moreover, to the polymer containing composition of the present invention, additives such as ultraviolet absorbers, antioxidants, surfactants and other various stabilizing agents may be added, in addition to the above.

[0049]

In the polymer containing composition of the present invention, there is used an amphiphilic block having, as a repeating unit structure, an alkenyl ether structure having at least one kind selected from an aromatic carboxylic acid, a carboxylic acid ester, and a carboxylic acid salt in which a hydrogen atom in a side chain in at least one block segment is substituted with a fluorine atom. Therefore, it is possible to form a high-order and fine structure. In addition, it is also possible to make a plurality of block segments have similar characteristics, thereby to more stabilize the characteristic thereof. For example, in a case where with the use of the above mentioned amphiphilic block polymer, a coloring material and water as a solvent are used to prepare a dispersion liquid, it is possible to include the coloring material within a micelle formed by the block polymer. In this manner, it becomes also possible to form a coloring material-inclusion ink composition. It is further possible to make the particles of a dispersing composition thereof even and uniform in size. Thus, it becomes also possible to make the dispersed state thereof highly stable.

[0050]

Next, an ink composition which is a preferred aspect of the composition of the present invention will be described.

The amount of the block polymer according to the first invention contained in the ink composition of the present invention is within a range from 0.1 to 90 mass%, and preferably within a range from 0.3 to 80 mass%. As the ink composition for use in an ink jet printer, the composition within a range from 0.3 to 30 mass% is preferably used.

[0051]

Next, components other than the block polymer contained in the ink composition of the present invention will be described in detail.

As other components, water, an aqueous solvent, a coloring material and an additive are included. The examples thereof have been given as mentioned above.

[0052]

As the coloring materials, pigments and dyes can be typically included. The pigments may be either organic or inorganic pigments. A black pigment and pigments of three primary colors, cyan, magenta and yellow may preferably be used for the ink. Incidentally, color pigments other than those described above, colorless or pale-color pigments, metallic luster pigments, and the like may also be used. Moreover, pigments which have been newly synthesized for the present invention may also be used. In addition, the pigments may be used in combination with the dyes.

[0053]

Examples of commercially available black, cyan, magenta and yellow pigments are shown below.

Examples of the black pigment include, but are not limited to, Raven 1060 (manufactured by Colombian Carbon Co.), MOGUL-L (manufactured by Cabot Corp.), Color Black FW1 (manufactured by Degussa AG) and MA100 (manufactured by Mitsubishi Chemical Corp.)

[0054]

Examples of the cyan pigment include, but are not limited to, C.I. Pigment Blue-15 : 3, C.I. Pigment Blue-15 : 4 and C.I. Pigment Blue-16.

[0055]

Examples of the magenta pigment include, but are not limited to, C.I. Pigment Red-122, C.I. Pigment Red-123 and C.I. Pigment Red-146.

[0056]

Examples of the yellow pigment include, but are not limited to, C.I. Pigment Yellow-74, C.I. Pigment Yellow-128 and C.I. Pigment Yellow-129.

[0057]

Moreover, pigments self-dispersible in water may also be used for the composition of the present invention. Such pigments dispersible in water include those of which dispersibility is enhanced utilizing a steric hindrance effect of a polymer adsorbed onto the surface thereof, or an electrostatic repulsion. Examples of such pigments that are commercially

available include CAB-0-JET200, CAB-0-JET300 (both manufactured by Cabot Corp.), and Microjet Black CW-1 (manufactured by Orient Chemical Corp.).

[0058]

5           The pigments used for the ink composition of the present invention are preferably contained in the amount of 0.1 to 50 mass% based on the total mass of the ink composition. If the content of pigment is less than 0.1 mass%, a sufficient image density cannot be  
10   obtained. In contrast, if the content of the pigment is more than 50 mass%, the fixation property of an image may be lowered. The content of the pigment is more preferably within the range of 0.5 to 30 mass%.

[0059]

15           Furthermore, the dyes may also be used for the ink composition of the present invention. Direct dyes, acid dyes, basic dyes, reactive dyes, water-soluble dyes for food pigments, insoluble pigments as disperse dye, and fat-soluble dyes can be used, which will be described  
20   below.

[0060]

Examples of the water-soluble dyes include direct dyes such as C.I. Direct Black -17, -62 and -154, C.I. Direct Yellow -12, -87 and -142, C.I. Direct  
25   Red -1, -62 and -243, C.I. Direct Blue -6, -78 and -199, C.I. Direct Orange -34 and -60, C.I. Direct Violet -47 and -48, C.I. Direct Brown -109, and C.I. Direct Green



-59;

acid dyes such as C.I. Acid Black -2, -52 and -208, C.I. Acid Yellow -11, -29 and -71, C.I. Acid Red -1, -52 and -317, C.I. Acid Blue -9, -93 and -254, C.I.

5 Acid Orange -7 and -19, and C.I. Acid Violet -49;

reactive dyes such as C.I. Reactive Black -1, -23 and -39, C.I. Reactive Yellow -2, -77 and -163, C.I. Reactive Red -3, -111 and -221, C.I. Reactive Blue -2, -101 and -217, C.I. Reactive Orange -5, -74 and -99, 10 C.I. Reactive Violet -1, -24 and -38, C.I. Reactive Green -5, -15 and -23, and C.I. Reactive Brown -2, -18 and -33; and

other dyes such as C.I. Basic Black -2, C.I. Basic Red -1, -12 and -27, C.I. Basic Blue -1 and -24, C.I. 15 Basic Violet -7, -14 and -27, C.I. Food Black -1 and -2. [0061]

Examples of the fat-soluble dyes include the following commercially available products for each color.

20 Examples of the black fat-soluble dye include C.I. Solvent Black -3, -22 : 1 and -50, but not limited thereto. [0062]

Examples of the yellow fat-soluble dye include C.I. 25 Solvent Yellow -1, -25 : 1 and -172, but not limited thereto.

Examples of the orange fat-soluble dye include C.I.



Solvent Orange -1, -40 : 1 and -99, but not limited thereto.

[0063]

Examples of the red fat-soluble dye include C.I.

5 Solvent Red -1, -111 and -229, but not limited thereto.

Examples of the violet fat-soluble dye include C.I.

Solvent Violet -2, -11 and -47, but not limited thereto.

[0064]

Examples of the blue fat-soluble dye include C.I.

10 Solvent Blue -2, -43 and -134, but not limited thereto.

Examples of the green fat-soluble dye include C.I.

Solvent Green -1, -20 and -33, but not limited thereto.

[0065]

Examples of the brown fat-soluble dye include C.I.

15 Solvent Brown -1, -12 and -58, but not limited thereto.

[0066]

The dye used in the ink composition of the present invention is contained preferably within a range from

0.1 to 50 mass% and more preferably within a range from

20 1 to 40 mass% relative to the total weight of the ink.

Although the above mentioned coloring materials are favorably used in the ink composition of the present invention, the coloring materials used in the ink composition of the present invention are not

25 limited to the above mentioned materials.

[0067]

As a solvent, any of water, aqueous solvents and

organic solvents may be used. Among them, water is preferably used. As water, ion exchange water from which metal ions and the like are removed, pure water and ultrapure water are preferable.

5 [0068]

In the ink composition of the present invention, the water is contained preferably in a range from 1 to 95 mass% and more preferably in a range from 5 to 90 mass%. With the content of the water in a range from 1  
10 to 95 mass%, the dispersing effect is more remarkably exhibited and a more uniformly dispersed state of the functional substance can be realized.

[0069]

Examples of the aqueous solvent used in the  
15 invention include: polyvalent alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol or glycerol; polyvalent alcohol ethers such as ethylene glycol monomethyl ether, ethylene glycol  
20 monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether or diethylene glycol monobutyl ether; and nitrogen-containing solvents such as N-methyl-2-pyrrolidone, substituted pyrrolidone or triethanolamine. In addition, monovalent alcohols such  
25 as methanol, ethanol or isopropyl alcohol can also be used to accelerate the drying of an aqueous dispersion on a recording medium.

[0070]

The aqueous solvent is contained in the ink composition of the present invention preferably within a range from 0.1 to 50 mass% and more preferably within  
5 a range from 0.5 to 40 mass%. When the content of the aqueous solvent is within the range from 0.1 to 50 mass%, the wetting effect is more remarkably exhibited and hence a more uniformly dispersed state of the functional substance can be realized.

10 [0071]

The amount of the above mentioned block polymer contained in the ink composition of the present invention is within a range from 0.1 to 90 mass% and preferably within a range from 0.3 to 80 mass% relative  
15 to the total weight of the ink composition. When the content of the block polymer is within the range from 0.1 to 90 mass%, the pigment contained in the ink composition of the present invention can sufficiently be disperse and hence the ink composition can exhibit  
20 an appropriate viscosity.

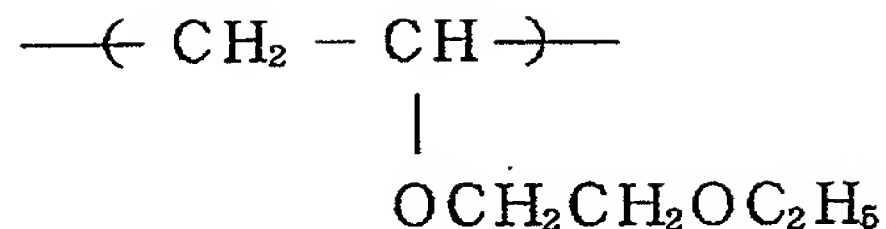
[0072]

Moreover, in the ink composition of the present invention, additives such as ultraviolet absorbers, antioxidants, surfactants, pH adjusters, penetrants,  
25 chelating agents and other various stabilizing agents may be contained, in addition to the above components.

[0073]

In addition to the above mentioned properties, the ink composition of the present invention may have a responsibility to stimuli. Owing to this stimulus responsibility, a stimulus is given to the ink composition in the course of formation of an image to increase the viscosity of the ink, whereby there can be afforded a favorable fixing property. As the stimulus, one stimulus which is appropriate to form the image is selected from temperature change, exposure to electromagnetic waves, pH change, concentration change and others, or appropriate stimuli are combined with one another. As a specific example, it has been confirmed from DSC that use of a temperature-sensitive stimulus responsible block polymer having a repeating unit structure represented by the following structural formula (3) induces phase transition of the block segment at about 20 °C as a border in an aqueous solution, and hydrophobicity is exhibited at a temperature higher than this border temperature and hydrophilicity is exhibited at a temperature lower than this border temperature. Therefore, such a stimulus responsibility can be afforded that when the block segment is cooled to a temperature lower than 20 °C, the block segment is made hydrophilic and extends, and hence polymer micells interacts with one another and an increase in viscosity is induced.

[0074]



5

[0075]

In a preferred aspect of the present invention, the ink composition is used as an ink composition of which characteristics are varied depending on a stimulus given thereto. The ink composition is high in pigment dispersing stability and is improved in bleeding and feathering occurred when the ink is adhered to a recording medium. In addition, the ink composition can be used as a pigment dispersing ink material which is excellent in fixing property and scratch resistance. Thus, the ink composition of the present invention which serves as the pigment dispersing ink material can be utilized as a high quality, low energy consumption and high speed image forming material.

[0076]

The polymer containing composition of the present invention is capable of changing its state (characteristics) responding to various stimuli. In the present invention, as the "stimuli", temperature change, electric field application, exposure to light

(electromagnetic waves) such as ultraviolet rays, visible rays or infrared rays, composition pH change, chemical substance addition and composition concentration change can be included.

5 [0077]

The ink composition of the present invention can be also favorably used as an ink for use in ink jet recording.

Next, a process of preparing an ink for use in ink jet recording in the present invention will be described.

[Process of Preparing Ink for Ink Jet Recording]

As the process of preparing an ink for use in ink jet recording of the present invention, there can be given, as an example, a process in which a pigment, the block polymer of the present invention, and an additive are added into ion exchange water and are dispersed by a disperser, and then, coarse particles are removed by a centrifugal separator, and then water or a solvent and an additive are added thereto, followed by stirring, mixing and filtration.

As dispersers, an ultrasonic homogenizer, a laboratory homogenizer, a colloidal mill, a jet mill, a ball mill and the like are available. The disperser may be used alone or used in combination with other dispersers.

[0078]

In addition, even in a case where a self-dispersing pigment is used, the ink can be prepared by operations similar to those in the above process.

Next, a liquid application method of the present invention will be described.

[0079]

[Liquid Application Method]

A preferred aspect of the ink composition of the present invention is a liquid application method of performing recording by ejecting the ink from an ink ejection portion and applying the ink thus ejected onto a recording medium. The ink application method is preferably used, in particular, in a pattern forming method of forming a predetermined pattern on a recording medium, various printing methods of forming images and characters/letters on recording media and various image forming methods such as an ink jet image forming method, an electrophotographic image forming method and the like. In particular, the liquid application method is more preferably used in the ink jet recording method.

[0080]

An ink jet recording method used may be a well known method such as a piezoelectric ink jet recording method using a piezoelectric element or a thermal ink jet recording method in which recording is performed by exerting thermal energy on ink to generate bubbles



therein. In addition, either a continuous type one or an on-demand type one may be used. Incidentally, the ink composition of the present invention can be also used in a recording system of printing an image with the ink on an intermediate transfer element and then transferring the image onto a final recording medium such as a sheet of paper.

[0081]

Next, an image forming apparatus of the present invention will be described.

[Liquid Application Apparatus]

The ink composition of the present invention can be used in a liquid application apparatus using the above mentioned liquid application method, a pattern forming apparatus using a pattern forming method of forming a predetermined pattern on a recording medium and image forming apparatuses using various printing methods of forming images and letters/characters on recording media and various image forming methods such as an ink jet image forming method, an electrophotographic image forming method and the like. In particular, the ink composition is more preferably used in the ink jet recording apparatus.

[0082]

The ink jet recording apparatus using the ink for ink jet recording of the present invention includes ink jet recording apparatuses of a piezoelectric ink jet



recording system using a piezoelectric element and a thermal ink jet recording system of performing recording by exerting thermal energy on the ink to generate bubbles therein.

5 [0083]

Fig. 1 shows a schematic functional diagram of an ink jet recording apparatus. In the figure, 50 denotes a central processing unit (CPU) of an ink jet recording apparatus 20. The program for controlling the CPU 50  
10 may be stored either in a program memory 66 or in memory means such as an EEPROM (not shown) serving as a so-called firmware. In the ink jet recording apparatus, the program memory 66 accepts record data from record data preparing means (not shown, a computer or the  
15 like). The record data may be the very information on images or characters/letters to be recorded, compressed information thereof or encoded information thereof. In a case that the compressed or encoded information is to be processed, information on the image or  
20 character/letter to be recorded can be obtained by making the CPU 50 execute expansion or explosion. The position of a head relative to a recording medium can be notified to the CPU 50 by providing an X encoder 62 (for example, encoding in an X direction or in a main  
25 scanning direction) and a Y encoder 64 (for example, encoding in a Y direction or in a sub-scanning direction).

[0084]

CPU 50 transmits a signal for recording the image to an X motor drive circuit 52, a Y motor drive circuit 54, and a head drive circuit 60 on the basis of the information from the X encoder 62 and the Y encoder 64. The X motor drive circuit 52 drives an X direction drive motor 56 and the Y motor drive circuit 54 drives a Y direction drive motor 58 to move a head 70 relative to the recording medium to a position where recording is performed. A head drive circuit 60 transmits signals for effecting discharge of various ink compositions (Y, M, C, K) or a stimulus giving substance serving as a stimulus to the head 70 at the moment that the head 70 has moved to the recording position to perform recording. The head 70 may be adapted to discharge a single color ink composition, or may be adapted to discharge a plurality of kinds of ink compositions, or may have a function of discharging the stimulus giving substance serving as the stimulus in combination with a function of discharging the ink composition(s).

[Example 1]

[0085]

Next, the present invention will be described in detail in relation to examples thereof. However, the present invention is not limited to these examples.

<Synthesis of Block Polymers>

Synthesis of a diblock polymer consisting of

isobutyl ether,  $\text{CH}_2 = \text{CHOCH}_2\text{CH}_2\text{OPhPh}$  : (IBVE-r-VEEtPhPh : A block), and 4-(2-vinyloxy)ethoxy-2,3,5,6-tetrafluorobenzonic acid ethyl (VEOEtPh(4F)COOEt : B block)

5 [0086]

The inside of a glass container equipped with a three-way cock was subjected to nitrogen substitution, and adsorbed water was eliminated by heating to  $250^\circ\text{C}$  under a nitrogen gas atmosphere. The system was  
10 returned to room temperature, and thereafter, 6 mmol (millimole) of IBVE, 6 mmol of VEEtPhPh, 16 mmol of ethyl acetate, 0.1 mmol of 1-isobutoxyethyl acetate, and 11 ml of toluene were added to the reaction system. Thereafter, the reaction system was cooled. When the  
15 temperature in the system was reached  $0^\circ\text{C}$ , 0.2 mmol of ethylaluminum sesquichloride (an equimolar mixture consisting of diethylaluminum chloride and ethylaluminum dichloride) was added to the reaction system, so as to initiate polymerization. Molecular  
20 weight was monitored by molecular sieve chromatography (GPC) in a time-division manner, and thus, completion of the polymerization of the A block was confirmed.

[0087]

Subsequently, 10 mmol of the B block monomer was  
25 added thereto, and the polymerization was continued. 24 hours later, the polymerization reaction was terminated. The polymerization reaction was terminated by adding

0.3% by mass of ammonia/methanol aqueous solution to the system. The reaction mixture solution was diluted with dichloromethane, and the diluted solution was washed with 0.6 M hydrochloric acid 3 times and then  
5 with distilled water 3 times. The obtained organic layers were concentrated and exsiccated with an evaporator, and the obtained vacuum-dried product was repeatedly dialyzed using a cellulose semipermeable membrane in a methanol solvent to eliminate monomeric  
10 compounds, so as to obtain a diblock polymer of interest. The compound was identified by NMR and GPC. As a result,  $M_n = 14,600$  and  $M_w/M_n = 1.32$ . The polymerization ratio (= compositional ratio) was A : B = 100 : 10. The polymerization ratio of two types of  
15 monomers was 1 : 1 in the A block.

[0088]

Thereafter, the thus obtained block polymer was hydrolyzed in a mixed solution consisting of dimethylformamide and sodium hydroxide water. Thus, the  
20 B block components were hydrolyzed, so as to obtain a diblock polymer that was converted into a sodium salt. The compound was identified by NMR and GPC.

[0089]

Thereafter, the compound was neutralized with 0.1  
25 N hydrochloric acid in a water dispersion solution, so as to obtain a diblock polymer wherein B components became free carboxylic acids. The compound was

identified by NMR and GPC.

[pKa Measurement of B Block]

3.0 mmol of an aliquot was picked up at a monomer unit of the B block components from the carboxylic acid-type block polymer obtained in Example 10. Then, distilled water was added thereto to obtain 50 g of aqueous solution in total. A 0.1N aqueous sodium hydroxide solution was added to the obtained aqueous solution, and the mixture was measured by potentiometric titration to obtain pKa. As a result, pKa = 2.2. The titration was carried out using an automatic titrater "COM-555" (manufactured by Hiranuma Sangyo Co., Ltd.)

(Example 2)

[0090]

15 parts by mass of the carboxylic acid salt-type block polymer obtained in Example 10 and 7 parts by mass of Oil Blue N (C.I. Solvent Blue-14 manufactured by Aldridge) were codissolved in 150 parts by mass of dimethylformamide. The resultant product was converted into an aqueous phase using 400 parts by mass of distilled water, so as to obtain an ink composition. Although the obtained ink composition was left for 10 days, the Oil Blue was neither separated nor deposited.

(Example 3)

[0091]

The printing head of an ink-jet printer (product

name: BJF800, manufactured by Canon Inc.) was filled with the ink prepared in Example 11, and recording was carried out. 1 minute after the recording, the printed portion was strongly scratched 3 times with a line  
5 marker, but tailing of blue color did not appear at all. Thus, it was found that the ink has extremely good fixability.

(Comparative Example 1)

[0092]

10           2 parts by mass of black self-dispersing pigment (product name: CAB-0-JET300, manufactured by Cabot Corp.), 0.5 part by mass of surfactant (Nonion E-230 manufactured by NOF Corp.), 5 parts by mass of ethylene glycol, and 92.5 parts by mass of ion exchange water  
15 were mixed to prepare an ink composition. Using the ink composition, recording was carried out in the same manner as in Example 3. 1 minute after the recording, the printed portion was strongly scratched once with a line marker. As a result, tailing of black color was  
20 observed.

[Industrial Applicability]

[0093]

The block polymer of the present invention is capable of satisfactorily dispersing a functional  
25 substance in a solvent and hence can be used as a polymer containing composition having good dispersion property for the functional substance. In addition, the

block polymer can be utilized as an ink composition which has good dispersion property for a coloring material and is excellent in printing and recording property. The ink composition is capable of being  
5 stably ejected from an ink jet recording apparatus to perform printing on a recording medium and hence can be used as an ink composition for use in an ink jet recording apparatus.

[Brief Description of the Drawing]

10 [0094]

[Figure 1] A schematic diagram showing the mechanism of an image forming apparatus of the present invention.

[Explanation of Reference Numerals]

[0095]

15 20: ink jet recording apparatus

50: CPU

52: X motor drive circuit

54: Y motor drive circuit

56: X direction drive motor

20 58: Y direction drive motor

60: head drive circuit

62: X encoder

64: Y encoder

66: program memory

25 70: head



[Name of the Document] Abstract

[Abstract]

[Object] To provide a polymer containing composition, in particular, an ink composition which has good  
5 dispersion property for a functional substance, in particular, a coloring material and which is excellent in printing and recording property, by using a block polymer capable of satisfactorily dispersing the functional substance in a solvent.

10 [Means for Attaining the Object] Provided is a block polymer having a repeating unit structure with an alkenyl ether structure including at least one kind selected from a carboxylic acid, a carboxylic acid ester and a carboxylic acid salt, each having a  
15 fluorine atom in a side chain in at least one block segment. The pKa of the carboxylic acid or the carboxylic acid salt is preferably 2.5 or less. Also provided is a polymer containing composition containing the above mentioned block polymer, a solvent or  
20 dispersion medium, and a functional substance. Further provided is an ink composition containing the above mentioned block polymer, a solvent or dispersion medium, and a coloring material.

[Suggested Figure for Publication] None



【書類名】図面

[Name of the Document] Drawing

【図1】

[Fig. 1]

